# METHOD FOR STORING HYDROGEN IN AN HYBRID FORM

## Field of the invention

The present invention relates to a method for storing hydrogen in a hybrid form. More specifically, it relates to a method for storing hydrogen in two different forms within a single tank.

The invention also relates to tanks hereinafter called “hybrid tanks”, which are specially adapted for carrying out the above method when the hydrogen is stored in liquid and solid forms and when the hydrogen is stored in solid and gaseous forms, respectively.

## BRIEF DESCRIPTION OF THE PRIOR ART

Methods for storing hydrogen can be classified in three main categories :

(A) gaseous storage in high pressure tanks ;

(B) liquid storage in cryogenic tanks ; and

(C) solid storage in tanks containing materials that absorb (in volume) or adsorb (on surface) hydrogen.

The last category listed above as category (C) is the one that makes use of metal hydride storage tanks.

Each of the above categories has advantages and disadvantages that are summarized in the following Table I :

**TABLE I**

**Characteristics of the different methods for storing hydrogen**

| Storing method | Advantages | Disadvantages |
|---|---|---|
| (A) Gaseous | • The filling and discharge kinetics (sec-min) is very fast<br>• The tanks made of composite material are of very light weight | • Very low storage capacity per volume unit and, accordingly, the necessity of using very large tanks<br>• Very high gas pressure is required to have a sufficient amount of hydrogen per volume unit (up to 10000 psi 690 bars)<br>• Significant loss of energy because mechanical compression is required to achieve the requested pressure level (15-20%)<br>• Risk of explosion or deflagration due to the very high pressure |
| (B) Liquid | • Excellent storage capacity per volume unit | • Problem of evaporation of liquid hydrogen (boil off)<br>• Significant loss of energy because refrigeration is required to reach the requested temperatures (30%) |
| (C) Solid (hydrides) "Hydrogen absorption in volume"<br><br>Solid (adsorbents) "Hydrogen adsorption on surface" | • Excellent storage capacity per volume unit which sometimes exceeds the one of liquid storage<br><br>• High storage capacity for some materials of high specific surface (activated carbon, etc...) | • Very low filling and discharge kinetics since the absorption and desorption of hydrogen is limited by the heat transfer (min-hr)<br>• Low storage capacity per weight unit because of the high weight of the absorbent material<br>• Significant loss of thermal energy for inducing hydrogen desorption (10-25%)<br>• Necessity of using very low temperatures (liquid nitrogen) to obtain a high storing capacity |

By way of example, in the case of a method for storing hydrogen in a gaseous form (category A), a tank of one (1) liter will contain the following amounts of hydrogen at the various pressures indicated in Table II :

**TABLE II**

**Gaseous storage**

| Hydrogen pressure | Amount of hydrogen within one liter |
|---|---|
| 3,600 psig (248 bar) | 0.0177 kg |
| 5,000 psig (345 bar) | 0.0233 kg |
| 8,000 psig (550 bar) | 0.0334 kg |
| 10,000 psig (690 bar) | 0.0392 kg |
| 15,000 psig (1,035 bar) | 0.0512 kg |

In the case of a method for storing hydrogen in a liquid form (category B), a tank of one (1) liter will contain 0.0708 kg of hydrogen since the density of liquid hydrogen at -252.8°C (that is at the conventional boiling point of hydrogen) is equal to 0.0708 kg/l.

Last of all, in the case of a method for storing hydrogen in a solid form with a metal hydride (category C), a tank of one (1) liter containing a hydride of formula $AB_5$ like $LaNi_5H_6$ (density: 6.59 kg/l, hydrogen storage capacity $\simeq$ 1.4%) occupying all the volume of the tank, will contain 0.0923 kg of hydrogen, that is almost twice the amount of hydrogen stored in a gaseous form in a tank of one liter at 15,000 psig.

The results of this comparative example are given in Table III :

## TABLE III

**Comparison of the storage capacity of the thru basic methods for storing hydrogen**

| Method | Amount of hydrogen stored within a tank of one liter |
|---|---|
| (A) Gaseous storage at 15,000 psig (1,035 bar) at ambient temperature | 0.0512 kg |
| (B) Liquid storage at -252.8C (1 bar) | 0.0708 kg |
| (C) Solid storage in a hydride of $LaNi_5$ (10 bar) at ambient temperature | 0.0923 kg |

Of course, in the case of the method for storing hydrogen in a liquid form (category B), there is always some gaseous hydrogen in equilibrium with the liquid because of some evaporation of the latter. Also, in the case of the method for storing hydrogen in a solid form with a metal hydride (category C) typically operating at low pressure (10 bar), there is some gaseous hydrogen because the hydride never occupies all the space in the tank. Moreover, in the case of the method for storing hydrogen in a gaseous form at a very high pressure (category A), there is always some hydrogen that is adsorbed (such adsorbed hydrogen is also called "solid hydrogen" according to the above terminology) onto the internal walls of the tank. Therefore, in each method listed hereinabove (gaseous, liquid and solid), there is always a small amount of hydrogen that is stored according to another method of storage.

By way of example, one may evaluate the maximum percentage of hydrogen that may come from another method of storage in the case of a tank of one liter containing a metal hydride powder ($LaNi_5H_6$). Assuming that the powder is not compacted and, therefore, occupies about half of the volume of the tank, that is about half a liter, considering also that the density of $LaNi_5H_6$ is equal to 6.59 kg/l and further assuming that the gaseous hydrogen within the

tank (about half a liter) is at a pressure 10 bar, the amount of hydrogen that is not solid within the tank of one liter will be as reported in Table IV:

**TABLE IV**

| "Gaseous" hydrogen (10 bar) | "Solid" hydrogen | Total amount of hydrogen |
|---|---|---|
| 0.00041 kg (0.9%) | 0.0462 kg (99.1%) | 0.0466 kg (100%) |

This example clearly shows that for any given method of storage, there can usually be 1% of hydrogen stored in a different form. However, in all cases, this amount will always be lower than 5% by weight.

It has already been suggested that there could be some advantages in coupling different means for storing hydrogen within a single category.

By way of example, U.S. patent No. 5,906,792 entitled "Nanocrystalline composite for hydrogen storage" in the name of the Applicant and the McGill University, discloses that there are advantages when one combines within a same tank a low temperature metal hydride with a high temperature metal hydride in contact with each other. When such a mixture is used for an internal combustion engine, the low temperature metal hydride allows cold starting of the engine by providing the hydrogen at the start up. When the engine is hot, the heat that is generated by the same permits to induce the desorption of hydrogen from the high temperature metal hydride (see column 3 of this U.S. patent No. 5,906,792 for more details).

Similarly, international laid-open patent application No. WO 01/16021 published on March 8, 2001 in the name of David G. SNOW et al, discloses that there are some advantages in combining solid storage in the volume (absorption) with solid storage on the surface (adsorption) in nanoparticles of a hydride in order to improve, *inter alia,* the hydrogen absorption and desorption kinetics.

U.S. patent No. 5,872,074 entitled « Leached nanocrystalline materials, process for manufacture the same and use thereof in the energetic field" in the name of the Applicant, also discloses that the hydrogen sorption

kinetics can be improved when use is made of a hydride having high specific surface.

Independently of the above, it is also known that the method (C) for storing hydrogen in a solid form usually has a response time (loading and unloading) much slower than the method (A) for storing hydrogen in a gaseous form and slower than the method (B) for storing hydrogen in a liquid form. Actually, at least 15 minutes and sometimes more than 1 hour are required to fill up a hydride storage tank. In spite of this drawback, the method for storing hydrogen in a solid form has the highest capacity of storage per volume unit (see again Table III hereinabove).

It is known that some technical applications require a response time much faster than one minute.

Thus, for example, in UPS systems (uninterruptible power supply) using fuel cells fed with hydrogen, a response time of about one hundred milliseconds is usually required. Of course, a hydrogen storing tank using metal hydride cannot satisfy this particular requirement. However, in such a case, use could be made of a tank in which hydrogen is stored in a gaseous form at high pressure.

Similarly, in hydrogen operated vehicles, there are different types of transitory periods, like :

short duration accelerations (second) which usually require a response time of about one hundred millisecond from the propulsion system; and

power increases when the vehicle is climbing up a hill, which may last a few minutes.

In hybrid vehicles which make use of a fuel cell and batteries, the very short accelerations (second) can be taken care by the batteries whereas the transitory periods of a longer duration (a few minutes) may require hydrogen stored in a gaseous form. On the other hand, the average power which is of about 20 KW for a typical vehicle, may easily be accomodated by a metal hydride tank. The energy contained in the batteries of such a vehicle usually represents about 1% of the energy on board. Therefore, one needs an amount

of hydrogen higher than 1% to take charge of the transitory periods.

To sump up, in view of the above, it is obvious that there is presently a major need for a method for storing hydrogen which would combine the advantages of the different methods listed hereinabove.

## OBJECT AND SUMMARY OF THE INVENTION

An object of the present invention is to satisfy the above mentioned need by providing a new method for storing hydrogen which combines the advantages of at least two of the above mentioned methods for storing hydrogen, namely the methods for storing hydrogen in a gaseous form, in a liquid form and in a solid form.

The present invention basically consists in coupling and using in a single tank hereinafter called « hybrid tank for storing hydrogen » at least two of the methods for storing hydrogen mentioned hereinabove, namely :

A) the method for storing hydrogen in a gaseous form ;

B) the method for storing hydrogen in a liquid form ; and

C) the method for storing hydrogen in a solid form, in volume or on surface.

The only condition is that each of the above methods is used for storing at least 5% by weight of the total amount of hydrogen within the tank.

Therefore, the invention as claimed is directed to a method for storing hydrogen in an hybrid form, which comprises the step of coupling and using within a single tank at least two hydrogen storage means selected from the group consisting of :

a) means for storing hydrogen in a gaseous form ;

b) means for storing hydrogen in a liquid form ; and

c) means for storing hydrogen in a solid form by absorption or adsorption,

with the proviso that each of the storing means that are used, is sized to store at least 5% by weight of the total amount of hydrogen stored within the tank.

The means mentioned hereinabove for storing hydrogen in different forms are those commonly used for carrying out each of the above mentioned methods. They are very conventional and need not be further described in detail. The only requirement is that they be coupled within the same tank in order to be used simultaneously for each storing at least 5% by weight of the hydrogen.

Another object of the present invention is to provide a hybrid tank for storing hydrogen in both liquid and solid forms, comprising two concentric containers, one of the containers hereinafter called "inner" container is located within the other one which is hereinafter called "outer container", the containers being separated by an insulating sleeve for maintaining the inner container at low temperature. The inner container is used for storing hydrogen in a liquid form. The outer container is in direct communication with the inner container and contains a metal hydride for storing hydrogen in a solid form.

A further object of the present invention is to provide a hybrid tank for storing hydrogen in both solid and gaseous forms, comprising:

- a container having a metallic liner or inner wall covered with a polymeric outer shell, said container being devised to store hydrogen in gaseous form at a higher pressure and to receive and store a metal hydride in order to store hydrogen in solid form;

- at least one heat pipe mounted within the container to allow circulation of a heat carrying fluid; and

- a heat exchanger located within the container in order to ensure thermal connection between said at least one heat pipe and the hydride.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The invention and the way it can be reduced to practice will be better understood upon reading the following non-limitative examples given with reference to the accompanying drawings in which :

Figure 1 is a diagram illustrating the equilibrium plateau of the hydride used in a hybrid gas-solid storage tank disclosed in example 1 ;

Figure 2 is a schematic cross-sectional view of the hybrid liquid-solid storage tank disclosed in example 2 ;

Figure 3 is a diagram illustrating the equilibrium plateau of the hydride used in the hybrid gas-solid storage tank disclosed in example 3 ;

Figure 4 is a schematic cross-sectional view of the hybrid gas-solid storage tank disclosed in example 3; and

Figures 5 and 6 are diagrams giving the equilibrium plateaux of several hydrides as a function of the temperature and indicating which one could be used in the hybrid gas-solid storage tank disclosed in examples 1 and 3.

**<u>EXAMPLE 1</u>: Hybrid storage tank for storing hydrogen in gas and solid forms**

A hydrogen storage tank having a volume of 1 liter has been filled up with a powder of nanoparticles of a hydride of $LaNi_5$ having an average diameter of 5 nanometers. The powder occupied 50% by volume of the tank, that is 0.5 liter, since it was not compacted. The number of atoms on the surface of these nanoparticles represented about 28% of the total amount of atoms within each particle considering a layer of 0.4 to 0.5 nanometer on the surface of each nanoparticle. The tank has then been filled up with gaseous hydrogen at different pressures ranging from 10 bar (typical pressure of use of the metal hydride tanks) to 700 bars (typical pressure used in high pressure gaseous tanks). It was assumed that the amount of hydrogen in the volume and at the surface of the metal hydride corresponded to H/M=1 (H = hydrogen, M = metal), which is typical to most metal hydrides. Under these conditions, the amounts of hydrogen associated to the two different means of storage that were used, have been calculated and are reported in Table V hereinafter :

**TABLE V**

| Hydrogen pressure within the tank | Hydrogen in gaseous phase (kg) | % | Hydrogen bound connected to the surface of the hydride | % | Hydrogen inserted within the hydride | % | Total amount of hydrogen (kg) |
|---|---|---|---|---|---|---|---|
| 10 bar * 150 psi | 0.0004 | 1 | 0.0142 | 28 | 0.0365 | 71 | 0.0511 |
| 248 bar 3600 psi | 0.0089 | 15 | 0.0142 | 24 | 0.0365 | 61 | 0.0596 |
| 345 bar 5000 psi | 0.0117 | 19 | 0.0142 | 23 | 0.0365 | 58 | 0.0624 |
| 690 bar 10000 psi | 0.0196 | 28 | 0.0142 | 20 | 0.0365 | 52 | 0.0703 |

It is worth noting that in the first case reported in Table V, that is when the pressure is of 150 psi (10 bar), the amount of hydrogen in gaseous phase represented about 1% of the total amount. This example is illustrative of what is presently obtained in conventional metal hydride tanks and is therefore outside the scope of the present invention. However, in the three other cases reported hereinabove where the pressures were of 3,600 psi, 5,000 psi and 10,000 psi, the amounts of hydrogen in gaseous phase represented about 15%, 19% and 28% respectively of the total amount of hydrogen within the tank. Such is much higher than the limit of 5% as indicated hereinabove.

The tank disclosed in example 1 is illustrative of a tank that can be used in a "back up" system based on a fuel cell or a hydrogen source generator. In the case of a failure of the electric supply, the hydrogen in the gaseous phase will initially supply the fuel cell or the generator that will slowly warm up. The pressure within the tank will be reduced. When the pressure reaches the equilibrium plateau of the hydride, that is about 2 bars for a $AB_5$ alloy at room temperature, there will be almost no more hydrogen in the gaseous phase. Then, the hydride will take over by providing hydrogen to the system thanks to the heat generated by the fuel cell or the generator.

It is worth noting that, in this example, the equilibrium plateau of

$LaNi_5$ which is a conventional low temperature metal hydride at the operating temperature (typically ranging between 0 to 100°C), is slightly higher than the pressure of hydrogen required at the inlet of the fuel cell, which typically about 2 bars. If the tank contains 50% by volume of hydride and the balance is occupied with gaseous hydrogen at 690 bars (10,000 psi), the situation will correspond to that of the diagram given in Figure 1.

Under such a circumstance, during operation of the system, the hydrogen will come first from the gaseous phase. Then, when the amount of hydrogen and the gas pressure become low, the hydride will take over by providing hydrogen to the system. The pressure within the tank will then be kept at the level of the desorption plateau of the hydride. The kinetics of the system will therefore be quite high at the beginning (response time of the gaseous system) and thereafter low (response time of the hydride system).

There are also other advantages in using such a hybrid method combining gas and solid storage. In particular, one can mention :

a) refilling up of the tank is carried out in a short time as compared to conventional metal hydride tanks ;

b) the design of the heat transfer components of the tank is simplified ; and

c) the high storage capacity by volume of the metal hydride and the high capacity of storage by weight of the new composite high pressure gas storage tanks are combined.

**<u>EXAMPLE 2 :</u> Hybrid tank for storing hydrogen in liquid and solid forms**

A hybrid tank 1 for storing hydrogen having a total volume of one liter has been devised from two concentric containers 3,5 (see Fig. 2). The inner container 3 had a volume of 0.8 liter whereas the outer container 5 had a volume of 0.2 liter. An insulating sleeve 7 was positioned between the inner and the outer containers 3,5 to keep the inner container 3 at low temperature.

In use, the inner container 3 of the tank 1 was filled up with liquid hydrogen. It contained about 0.0708 kg/l x 0.8 liter = 0.0566 kg of hydrogen. The

outer container 5 was filled with a powder of a metal hydride of the type $LaNi_5H_6$ which occupied about 50% of the volume, that is about 0.1 liter. Therefore, the outer container 5 contained 6.59 kg/l x 0.1 liter x 1.4% = 0.0092 kg of hydrogen. The total amount of hydrogen stored within the tank 1 was equal to 0.0658 kg (14% in the outer tank and 86% in the inner tank).

As compared to a conventional tank for storing hydrogen in a liquid form, the tank disclosed in example 2 has the advantage of having no loss of hydrogen over a period that may exceed two weeks. Indeed, the problem with any conventional liquid hydrogen storage tank is that the hydrogen evaporates (boil off). Up to 1% of the amount of liquid hydrogen can evaporate each day from a conventional tank (1% x 0.0566 kg = 0.0006 kg/day). In the hybrid tank disclosed in example 2, the boil-off hydrogen is absorbed by the metal hydride that extends in periphery of the inner container and up to its maximum capacity (that is 0.0092 kg/0.0006 kg/day = 15 days).

It is worth noting that the idea of using metal hydrides for "catching" evaporated hydrogen from a liquid hydrogen storage tank has already been suggested, but by means of two separate systems that must be interrelated, connected and independently controlled. In this regard, one can refer to U.S. patent No. 5,728,483 to SANYO ELECTRIC CO. In contrast, in the present invention, these two different means for storing hydrogen are combined within a single tank and therefore operate in a simpler manner.

## <u>EXAMPLE 3 :</u> Hybrid tank for storing hydrogen in gas-solid form for use in a system having transitory periods

In the tank disclosed in example 1, use was made of $LaNi_5H_6$ as the hydride. This compound is known to have a low equilibrium plateau (*viz.* lower than 40 bar) at operating temperature. Use could also have been made of other hydride with a low equilibrium plateau, such as $NaAlH_4$, $LiAlH_4$ or $MgH_2$.

According to the invention, it is however possible to use also a hydride having an equilibrium plateau that is much higher at the operating temperature (typically ranging between 0° and 100°C) than the equilibrium

plateau of the conventional hydrides (typically ranging between 1 to 10 bar). Such a high equilibrium plateau is 40 bar or higher . An example of such hydrides is $TiCr_{1.8}$ which has an equilibrium plateau at room temperature much higher than 100 bars (see Fig. 6). There are also medium temperature hydrides with equilibrium plateau at high pressures, like $TiMn_{2-y}$, $Hf_2Cu$, $Zr_2Pd$, $TiCu_3$ or $V_{0.855}Cr_{0.145}$ which can be of interest for this kind of application (see Figs. 5 and 6).

Under these circumstances, when there is a need for hydrogen, the gaseous system of the storage tank will permit to accommodate such a request with a very short response time (t1) of about one second (for example in the case of a car that accelerates). When the pressure within the tank drops and changes from a value (1) to a value (2) (see Fig. 3), the hydride will regenerate the gaseous system with a lower response time (t2) of a few minutes, until the next acceleration.

This hybrid method makes it possible to substantially simplify the structural components required for heat transfer in order to induce the desorption from the hydride or absorption therein. Moreover, this hybrid method permits, thanks to the high pressure, to solve the problem of refilling hydrides such as the alanates ($NaAlH_4$ or $LiAlH_4$). As to the kind of hydrides that can be used, reference can be made to Figure 5 (hydrides of the $AB_5$ type) and Figure 6 (hydrides of the $AB_2$ type) enclosed herewith.

As an example of the way this method could be carried out, reference can be made to Figure 4 which shows a hybrid tank 11 for storing hydrogen in both solid and gaseous form. The tank 11 comprises a container having a metallic liner or inner wall 15 covered with a polymeric outer shell 13. This type of container is conventional and commonly used for storing hydrogen in gaseous form at high pressure. It is preferably cylindrical in shape and provided with an axial opening 17. The liner 15 is usually made of aluminium whereas its outer shell is made of a composite material reinforced with carbon fibers. In practice, the container of the hybrid tank 11 is intended to be used for storing hydrogen in gaseous form at a pressure usually higher than 40 bar and

simultaneously to receive and store a metal hydride in order to store hydrogen in solid form as well.

At least one heat pipe 19 is mounted within the container to allow the circulation of a heat carrying fluid within the container 11. As shown, the tank 11 preferably comprises only one heat pipe 19 which is inserted into the container through the opening 17 and extends axially within the same. The tank 11 further comprises a heat exchanger located within the container to ensure thermal connection between the heat pipe 19 and the hydride. This heat exchanger preferably consists of at least one metallic grid, or a porous metallic structure or fibers 21 which extends transversally within the container and is in direct contact with the axial heat pipe 19, the metal liner wall 15 of the container, and the hydride stored within the same.

The use of such a system of heat pipe and heat exchanger to operate a metal hydride is already known (see, for example, U.S. patent No. 6,015,041 granted in 2000 in the name of WESTINGHOUSE SAVANNAH RIVER CO). In the present case, the invention essentially lies in that the incorporation of such a system into a tank used so far only for storing hydrogen in a gaseous form at high pressure in order to benefit from the advantages of both technologies simultaneously.